Dielectric measurements of nematic and smectic A phases in a binary system

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The phase diagram of a binary mixture of 4-*n*-octyloxy-phenyl–4′-*n*-heptylcyclohexane carboxylate (molecule having weak polar terminal group) and 4-nitrophenyl-4′-*n*-pentylbenzoate (molecule having strong polar terminal group) has been studied using polarizing microscope and differential scanning calorimeter. The phase diagram shows an enhancement in smectic A phase over a wide composition range and intermediate nematic phase in a narrow composition range. The dielectric properties of these phases are investigated in the frequency range of 100 Hz to 1 MHz.

Liquid crystals are anisotropic fluids with partially ordered phases and are thermodynamically between an isotropic liquid and three dimensional ordered crystal. They show a variety of phases, viz., nematic (N), smectic A (Sm A) and smectic C (Sm C) and the chiral analogous of nematic (N*) and smectic C (Sm C*). Usually, multicomponent mixtures are formulated for a liquid crystalline phase to exist over a broad temperature range. This facilitates not only in lowering of the melting point when eutectic composition is prepared, but also to adjust the physical properties of mixtures such as viscosity, birefringence, permittivity, etc. Normally a mixed system should behave in an ideal manner predicted from the theory of ideal solutions but often positive deviations in the curves of phase transitions are observed, i.e., the liquid crystalline phases existing in pure compounds, in bi-component or even in multi-component systems enhance their own thermal stability[1-9]. Sometimes, new phases of higher order are also induced. Induced nematic and smectic phases have also been observed in discotic systems[10,11] by doping them with non-liquid crystalline materials. Thus, the phase study of mixture of liquid crystalline

materials has become a rich area for investigation by the theoreticians as well as by experimentalists.

The reorientation of molecules in liquid crystalline phases have been studied[12,13] by various methods, viz., dielectric spectroscopy, neutron scattering, etc. In liquid crystalline phases, the dielectric constants are important parameters for technical applications and reflect the relationship of permanent dipole and molecular polarizability in the respective phases. Additionally, based on dielectric relaxation data, it can be established that in the nematic phase the molecules reorient around the short axes as well as around the long axes. These two motions differ largely in their time characteristics as the former occurs with a relaxation time of 10^{-8} s whereas in the latter the relaxation time is approximately 10^{-10} s.

Herein, we report the results of dielectric studies carried out on a binary mixture which shows enhancement and thermal stability to smectic phase and also appearance of an intermediate phase. The purpose of these studies is to investigate experimentally if the activation barrier for molecular rotation around short axes is smaller in the smectic A phase than in the nematic phase. The microscopic, calorimetric and dielectric investigations have been carried out to study these peculiarities of the binary system.
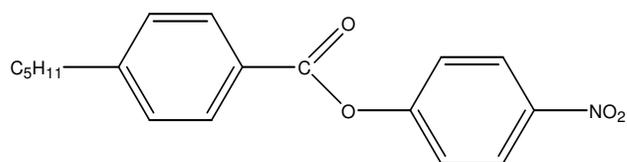
Experimental

The following compounds were investigated in the present study:

1. 4-*n*-Octyloxyphenyl–4′-*n*-heptyl cyclohexane carboxylate (D-7O8)
    Cr 44.0 Sm B 67.0 Sm A 78.0 N 81.1 I
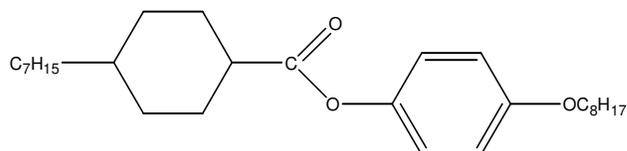
2. 4-Nitrophenyl-4′-n-pentylbenzoate (NPPB)
    Cr 62.0 I

The symbols used are Cr: crystalline solid; Sm A: smectic A phase; Sm B: smectic B phase; Sm E: smectic E phase; N: nematic phase and I: isotropic liquid. Temperatures are in °C.

The isobaric phase diagram of binary system NPPB/D-7O8 was studied using a Leitz polarizing microscope equipped with a Mettler FP 82 hot stage and Mettler FP 90 central processor in the heating as well as cooling modes. Mesophases and their corresponding phase transition temperatures were primarily determined by the use of thermal optical microscopy of liquid crystalline material layered between two untreated glass plates. The phase transitions were further confirmed by differential scanning calorimetric studies on a Perkin Elmer scanning calorimeter maintaining the rate of heating as well as cooling at 2 °C per minute.

The dielectric study was performed in the frequency range of 100 Hz to 1 MHz using a Solartron Schlumberger impedence analyzer Si 1260 and the Chelsea interface. A brass cell coated with gold (d = 0.1 mm) was used as the capacitor which was calibrated with cyclohexane. The compound was oriented using a magnetic field of 0.6 T parallel (p) and perpendicular (s) to the nematic director. The magnetic field was kept constant during cooling.

The experimental point of dielectric function, $\varepsilon*(f) = \varepsilon'(f) - j\varepsilon''(f)$, were fitted to the following equation which consists of the Cole–Cole term (term 2), a conductivity contribution (term 3) and term 4 for the description of double layer at lower frequencies,

$$\varepsilon^*(f) = \varepsilon_1 + \frac{\varepsilon_0 - \varepsilon_1}{(1 + j\varpi\tau_1)^{1-\alpha}} - \frac{jA}{f^M} + \frac{B}{f^N} \qquad \ldots (1)$$

where ε_0 and ε_1 are low and high frequency limits of the dielectric constant respectively, $\omega = 2\Pi f$ (f is frequency), τ_1 is the relaxation time and α is the Cole-Cole distribution parameter. The conductivity term A ($\kappa = 2A\Pi\varepsilon^0$, $\varepsilon^0 = 8.85 \times 10^{-12}$ A s V^{-1} m^{-1}, if N = 1) and M, B and N are further fit parameters describing the slope of the conductivity and capacity of the double layer.

Results and discussion

Structurally, NPPB is a liquid crystalline material but polymorphically does not show any liquid crystalline phase transition. It melts at 62.0 °C into isotropic liquid. D-7O8 belongs to the D-nOm series[14] (where n and m refers to the alkyl and alkyloxy substituents on left and right sides of the molecule shown in compound 1).

The phase diagram for the system presented in Fig. 1 has been constructed using polarizing microscope and differential scanning calorimeter data. The successive addition of D-7O8 makes the appearance of an intermediate nematic phase at about 10 weight % of D-7O8 which continues till 25 weight %. A regular enhancement in smectic A – isotropic transition temperature is also seen, the maximum of which is observed at 87.0 °C. The intermediate nematic phase is immiscible with the nematic phase of D-7O8 while the smectic A phase has been found to exist over a wide concentration range. Therefore, we considered it worthwhile to study the dynamic behavior of intermediate nematic and enhancement of smectic A phase at the selected compositions. For this purpose, two different compositions, i. e., 13.44 % of D-7O8 and 50.9 % of D-7O8 were chosen and their DSC and dielectric studies were carried out.

The DSC curve of 13.44 % mixture of the binary system confirms phase transition from nematic phase to the isotropic state. However, super cooling of the phase transition, which is a routine feature of crystallization, is observed on lowering the temperature. The microscopic observations together with the DSC data agree very well for all the composition ranges selected in the Fig. 1.

The dielectric measurements made for this composition are shown in Fig. 2 as a plot of dielectric constant versus temperature. The DSC and dielectric data together prove phase transition from nematic phase to the isotopic state. The dielectric constant remains nearly uniform in the isotropic state in both,
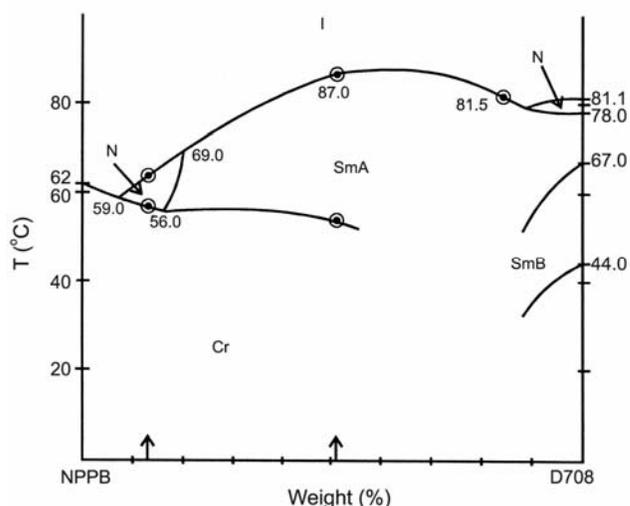

Fig. 1 — Isobaric phase diagram for the binary system of components NPPB and D-7O8. [Measurements have been carried out at the temperature indicated by the arrows].

parallel as well as perpendicular, orientations. An abrupt change in the dielectric constant in both the orientations is visible when the nematic phase begins to appear in the isotropic melt, giving rise to an overall positive dielectric anisotropy, $\Delta\varepsilon = \varepsilon_{0p} - \varepsilon_{0s}$, caused by the considerable longitudinal dipole moment. The perpendicular component of dielectric constant decreases on decreasing the temperature indicating that the molecular dipole contributes less in this orientation at low temperatures. The sign of dielectric anisotropy in the microwave frequencies can be qualitatively explained by taking into account the Maier-Meier[15] formula obtained by modifying the Onsager theory[16] of dielectric properties of isotropic liquids to nematics for a binary system[17]. This is characteristic for strongly polar substances which is comparable with the anisotropies obtained for other compounds[18,19].

The average values of dielectric constant, which can be calculated as $\varepsilon_{av} = (\varepsilon_{0p} + 2\varepsilon_{0s})/3$, is found to be slightly lower than that of the isotropic value. This is in accordance with the theory and results reported by the earlier researchers[20-22]. However, as the nematic phase begins to crystallize, a considerable change in the dielectric constant is seen. Since the molecular motions are now completely frozen, the dielectric constants in the two orientations remain constant. Further, it may be pointed out that the data has been obtained on cooling the sample and sufficient time has been given for stabilizing the phase at a given temperature.

The dependence of the real and imaginary parts of the dielectric permittivity ε' and ε'', fitted using the model described by above equation, is given in Fig. 3. It was not necessary to consider the data in the isotropic state since no dispersion in the dielectric permittivity was observed. However, in the nematic phase the relaxation mode is observed corresponding to the higher frequencies in the parallel orientation. For the perpendicular oriented nematic sample, the relaxation spectrum is, probably, shifted to larger frequencies.

For the parallel orientation, the relaxation phenomenon has been indicated by the peak of the curve which shows that maximum absorption takes place in the vicinity of 10^6 Hz at different temperatures in the nematic phase[23-24]. Using this data, the corresponding relaxation time, τ, has been calculated from the expression $\tau = 1/2\Pi f$ where f is the relaxation frequency. The variation of relaxation time with temperature (Table 1) ranging from
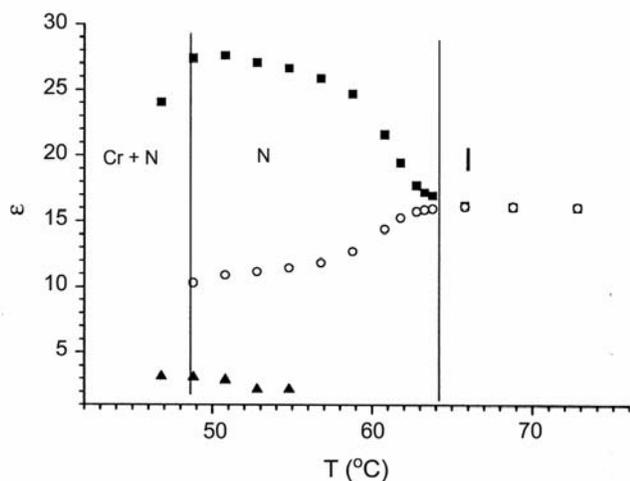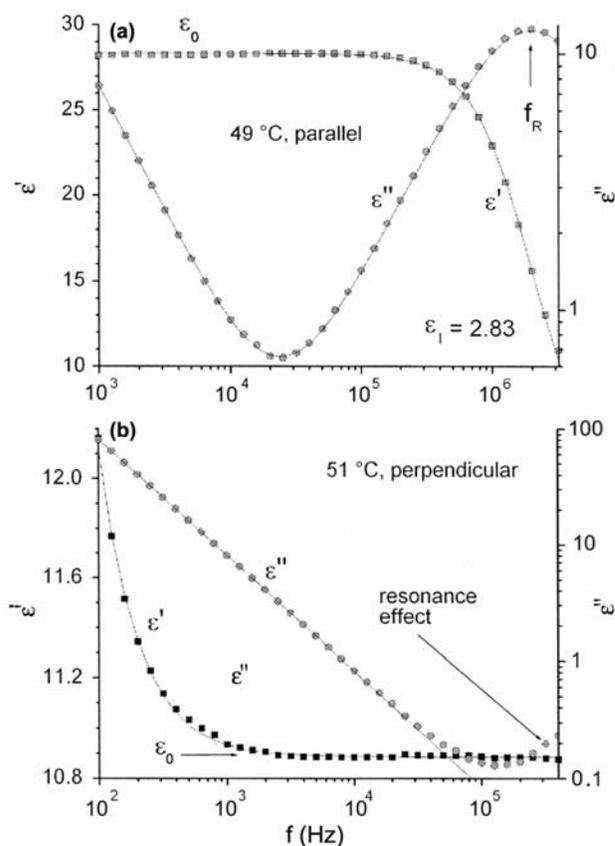

Fig. 2 — Dielectric permittivity parallel (p) and perpendicular (s) to the nematic director for 13.44 % mixture of the binary system NPPB/D-7O8. [■, Parallel orientation ε_{0p}; ○, Perpendicular orientation ε_{0s}; ▲, Data corresponding to relaxation phenomenon].

Fig. 3 — Real and imaginary parts of dielectric permittivity (ε' and ε'') as a function of frequency in the nematic phase in (a) parallel orientation at 49 °C and (b) perpendicular orientation at 51 °C. [■, Dielectric absorption curve (ε'); ○, Dielectric dispersion curve (ε'')].

9.93×10^{-8} s to 5.15×10^{-8} s, between 47 °C and 55 °C in the nematic phase, gives mean activation energy of 73±6 kJ/mol.

These values are in agreement with the values reported for the pure nematogens as well as in binary mixtures[25,26]. It may be noted that increase in ε'' at higher frequencies in the perpendicular direction is caused by the resonance effect.

Another interesting feature in the system (Fig. 1) is the enhancement of smectic A phase in the middle concentration. This phase builds its region of existence from 20 % of D-7O8 onwards; the maximum temperature observed using clubbed measurements being around 87 °C. In order to study the dynamic behaviour of this phase, dielectric measurements were carried out for 50.9 % mixture of D-7O8. Figure 4 shows the limits of dielectric permittivity as a function of temperature in the isotropic and smectic A phases calculated from the experimental data according to Eq. 1.

This behaviour is typical for most of the binary systems studied[24,27]. A considerable drop in the permittivity is observed at the I-Sm A phase transition. The two vertical bars show a biphasic region of isotropic and nematic phases within which the permittivity shows an abrupt downward jump. The static permittivity in the isotropic phase for this mixture is considerably lower than the static permittivity observed in the mixture

containing nematic phase (Fig. 2). This may lead to the conclusion that the dipole moments exhibit anti-parallel correlations in the isotropic phase of the mixtures. Within the smectic phase the permittivity is practically constant. Due to the lack of nematic phase in this composition, the substance could not be oriented. The dielectric absorption (ε') and dispersion (ε'') data in smectic A phase is presented in Fig. 5.

In the smectic phase, the measurements up to the selected frequency reveal relaxation process occurring near high frequency. The large value of ε_1 suggests that in this case the relaxation process is connected with rotation of molecules. The relaxation time in the smectic phase (Table 1) gives an average value of activation energy as 53±4 kJ/mol. Also, the specific conductivity calculated from the observed data shows well defined steps typical of a first order phase transition (Fig. 6). The point of intersection between

Table 1 — Relaxation time calculated for different phases

Nematic phase

T (°C)	47	49	51	53	55
τ (10^{-8} s)	9.93	8.65	7.41	6.06	5.15

Smectic A phase

T (°C)	42	48	52	56	60
τ (10^{-8} s)	16.33	10.94	9.14	7.04	5.38

Fig. 5 — Real and imaginary parts of dielectric permittivity (ε' and ε'') as a function of frequency in smectic A phase at 42 °C. [■, Dielectric absorption curve (ε'); O, Dielectric dispersion curve (ε'')].
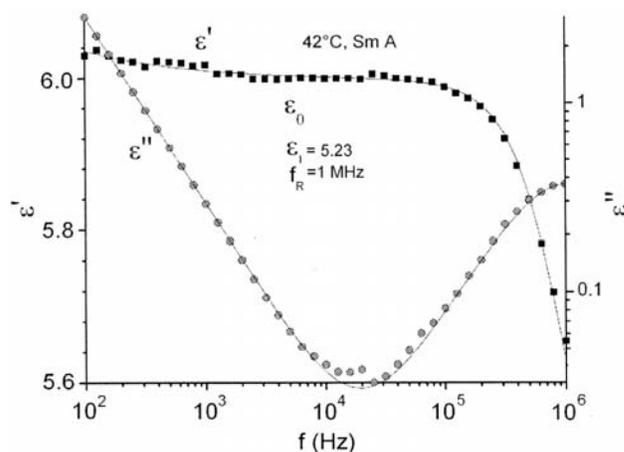

Fig. 4 — Dielectric permittivity in smectic A phase for 50.9 % mixture of the binary system NPPB/D-7O8. [●, ε_0; ▲, ε_1].
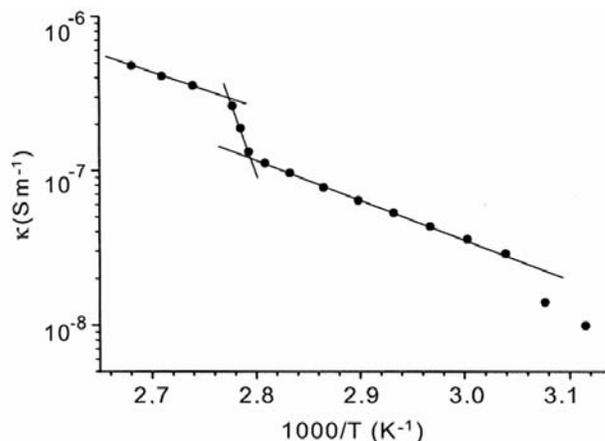

Fig. 6 — Specific conductivity as a function of reciprocal temperature for the given concentration.

the two slopes indicates a biphasic isotropic + smectic A region. At low temperatures, the change in conductivity is due to the formation of critical size nuclei, typical of crystallization.

In the above study, the binary mixture of NPPB/D-7O8 shows smectic A phase in a wide temperature range as well as composition range with a nematic "island" formed in the composition rich in polar component. It does not show any miscibility with the enantiotropic nematic phase of D-7O8. The dielectric anisotropy and its variation with temperature is positive and quite high in the intermediate nematic phase. Both smectic A and nematic phases show low frequency relaxation phenomenon. Taking into account the fitting of the dielectric data, dependence of relaxation frequencies and values of activation energies in nematic and smectic A phases, it may be concluded that the relaxation phenomenon is undoubtedly connected with rotation of individual molecules about their short axes.

Acknowledgement

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